WAVE LENGTHS LONGER THAN 5500 A IN THE ARC SPECTRA OF YTTRIUM, LANTHANUM, AND CERIUM AND THE PREPARATION OF PURE RARE EARTH ELEMENTS

CONTENTS

PART I.—WAVE LENGTHS LONGER THAN 5500 A IN THE ARC SPECTRA OF YTTRIUM, LANTHANUM, AND CERIUM

	Page
I. Introduction	318
II. Apparatus and methods	319
III. Results	321
1. Yttrium	321
2. Lanthanum	323
3. Cerium	326
IV. Summary	335

PART II.—THE PREPARATION OF PURE RARE EARTH ELEMENTS

I. Introduction	337
II. The cerium group	338
1. Cerium	338
2. Samarium	339
3. Lanthanum	341
4. Neodymium	342
5. Gadolinium	342
III. The yttrium group	344
1. Yttrium	344
2. Dysprosium	348
3. Erbium	350

PART I.—WAVE LENGTHS LONGER THAN 5500 A IN THE ARC SPECTRA OF YTTRIUM, LANTHANUM, AND CERIUM

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ABSTRACT

This paper contains the results derived from a study of the yellow, red, and infrared regions of the arc spectra of yttrium lanthanum, and cerium. Spectrograms were photographed with the dyes pinacyanol. kryptocyanin, and dicyanin. The rare earth compounds studied were derived from two sources: From the University of Illinois were obtained the oxalates of yttrium and lanthanum and the oxide of cerium, prepared under the direction of Prof. B. S. Hopkins; from Eimer and Amend were obtained the chlorides of yttrium and lanthanum and the nitrate of cerium, the last being a Kahlbaum preparation. In addition to spectrograms of the above-named materials secured with the concave grating spectrograph of the Bureau of Standards there were available for measurement two spectrograms made by Dr. Eder, of Vienna, with his grating spectrograph. These spectrograms were of yttrium and cerium salts prepared by C. Auer von Welsbach. The tables submitted herewith contain about 175 lines in the spectrum of yttrium, 410 in the spectrum of lanthanum, and about 1700 in that of cerium. Many of the wave lengths are those of heads of bands which are prominent in the spectra of yttrium and lanthanum. Part II of this paper, prepared by Prof. B. S. Hopkins and Dr. H. C. Kremers at the University of Illinois, describes the methods used in purifying the samples of yttrium, lanthanum, and cerium, which were used in this work.

I. INTRODUCTION

The rare earths present many interesting problems not only to the chemist, but to the spectroscopist as well. Indeed, the chemist, in separating and purifying his various preparations of the compounds of the rare earth metals, avails himself to a great extent of spectroscopic methods. And in one instance, at least, the spectroscopist has indicated the presence of a new and unsuspected element which had escaped detection by the chemist.[1]

In addition to its work of measuring standard wave lengths in the spectra of the chemical elements, the spectroscopy laboratory at the Bureau of Standards makes frequent spectroscopic analyses of various metals, salts, alloys, etc., to ascertain their composition and purity. The opportunity which arose when a number of samples of rare earth compounds (prepared at the University of Illinois by Prof. Hopkins and his coworkers) were submitted for

[1] Kaiser, Akad. der Wiss. Sitz. Wien., 126, IIa, p. 473; 1917.

analysis was taken advantage of to study the yellow, red, and infra-red regions of their arc spectra. This work was done in continuation of a program which was begun several years ago and is now well on the way toward completion. This program has as one of its objects the mapping of the red and infra-red spectra of the chemical elements as far out into the region of longer wave lengths as modern photographic methods will permit. To date results for about 35 elements have been published,[2] and work on the remainder is in various stages of progress. This paper presents the data derived from a study of the arc spectra of yttrium, lanthanum, and cerium. Wave lengths in the spectra of other rare earth elements have been measured and will be published as soon as the work of compiling the tables is completed.

II. APPARATUS AND METHODS

Most of the spectograms upon which the present study is based were secured with the concave grating spectograph of the Bureau of Standards. This instrument has been described in a previous publication.[3] Four gratings, all ruled at the Johns Hopkins University and of 640 cm radius, were used in the spectrograph. The third order of a grating ruled with 10 000 lines to the inch, was used in photographing the regions of the spectra between 5500 A and 5900 A. The dispersion was 2.3 A per millimeter. The first orders of two 20 000 lines-per-inch gratings (dispersion 3.6 A per millimeter) were used to photograph the spectral regions between 5500 A and 8000 A. For the region from 8000 A to 10 000 A the first order of the 7500 lines-per-inch grating, regularly in use in this laboratory, was employed. A few spectrograms in shorter wave-length regions were also made in the third and fourth orders of the last-named grating.

The materials whose spectra were studied were derived from two sources. From Eimer and Amend were obtained the chlorides of yttrium and lanthanum and the nitrate of cerium, the last named being a Kahlbaum preparation. As mentioned above, several preparations of rare earths were received for analysis from the chemistry department of the University of Illinois. Among these were the oxalates of yttrium and lanthanum and the oxide of cerium. A statement of the methods of extracting these compounds from their ores and purifying

[2] B. S. Bull., 14, pp. 371, 637, 765, 1918; B. S. Scientific Papers, 15, p. 251, 1919; 16, p. 51, 1920. Also Popular Astronomy, 29, p. 18; 1921.

[3] B. S. Bull., 14, p. 373; 1918.

them has been prepared by Profs. Hopkins and Kremers and constitutes the second part of this paper.

The salts were vaporized either on graphite or copper electrodes, the latter, however, being used for the greater portion of the work. Although the spectrum of copper has some strong lines in the regions studied, yet it is believed that few lines, if any, in the spectra examined have been omitted because of coincidence with copper lines. We have found the use of copper preferable to the use of graphite because of the steadiness with which the copper arc burns, especially when a bead from the upper electrode is fused with the metal in the lower. The advantage of this feature in the case of long exposures can be appreciated. Current strengths of 6 to 10 amperes were used under 240 volts pressure, depending on the spectral region being photographed.

The spectrograms were made on Seed 23 and Seed 30 plates measuring 2½ by 8 inches. They were sensitized to the yellow, red, and infra-red regions of the spectrum with pinacyanol, kryptocyanin,[4] and dicyanin, respectively. Dyes produced in this country and abroad were used with equal success. The exposure times ranged from 2½ minutes for the yellow regions to 5 hours for the infra-red. The arc spectrum of iron served as comparison spectrum, and its wave lengths determined by interference methods[5] were used in the reductions. The iron spectrum was photographed both at the beginning and at the end of long exposures in order to eliminate any possible temperature shift. Inasmuch as the grating is mounted in a small room whose temperature changes are gradual through long periods of time, corresponding to seasonal changes, no trouble from this source was experienced. A potassium bichromate cell or a screen of red glass, Jena 4512, was used in front of the slit of the spectrograph to remove overlapping higher orders of spectra.

In addition to the spectrograms made here, as described above, the Bureau of Standards has received from Prof. J. M. Eder, of Vienna, a number of spectrograms of the rare earth preparations of C. Auer von Welsbach. Among them, two—one of erbium nitrate containing yttrium, the other of cerium chloride—extend into a portion of the same spectral regions investigated here. These spectrograms were secured by Eder with a Rowland concave grating of 4.6 m radius and containing 13 000 lines per inch. The

[4] J. Op. Soc. of Am., 4, p. 91, 1920; J. Am. Chem. Soc., 42, p. 2661, 1920.
[5] B. S. Bull., 13, p. 245, 1916.

dispersion was 3.7 A per millimeter. The results derived from these plates are included with those given in the tables of this paper.

All the plates were measured on a large engine of which the smallest scale division is 0.001 mm. The spectrograms were measured directly in the sense increasing wave lengths with increasing scale readings, and then in the reversed position. In both directions of measurement from two to six settings with the micrometer wire were made on each line according to its sharpness.

III. RESULTS

In the following tables are brought together the results derived from the measurement of the plates. The tabulated wave lengths are, in the case of yttrium and lanthanum, the averages of from 2 to 12 determinations, and in the case of cerium, from 2 to 7. The majority of the tabulated wave lengths, however, are the means of 4 observations. Lines observed only once were recorded on plates exposed longer than the average to a particular spectral region.

The second and third columns of the tables give symbols describing the intensity, character, and accuracy of the lines. The intensities range from 1 or <1 for the faintest lines measured to 10 for the strongest. An asterisk (*) in the second column denotes that the line was not observed in the spectra of the preparations submitted by the University of Illinois. Lines so marked may be due to impurities, but it is very probable, since most of them are faint, that they failed to appear on the spectrograms because the exposures were not sufficiently long. The letters and symbols in the explanatory columns have the following significance:

b=broad.
coin=coincident.
d=double.
g=ghost.
h=hazy.
l=shaded to red.
n=band head.
p=part of band structure.
R=reversed.
v=shaded to violet.
A=probable error of 0.000 A to 0.010 A.
B=probable error of 0.010 A to 0.020 A.
C=probable error of 0.020 A to 0.030 A.
D=probable error >0.030 A.
E=only one determination.

Lines with probable errors A and B were measured three times or more.

1. YTTRIUM

About 175 lines in the arc spectrum of yttrium were measured between the limits 5503 A and 7882 A. Of these, approximately

one-fifth are the heads of bands which form a prominent feature of the orange and red regions of the yttrium spectrum. Prolonged exposures, up to five hours in length, failed to show any lines in the spectrum beyond that at 7881.87 A.

The yttrium oxalate received from the University of Illinois was very pure, the only impurities present, if any, being indicated by several faint lines which occur also in the spectra of lanthanum or erbium. These lines are marked in the second column of Table 1. The yttrium chloride received from Eimer and Amend contained a considerable amount of calcium, but was uncontaminated by other rare earths.

An extensive study of the spectrum of yttrium has been made by Eder.[6] Using yttrium sulphate prepared by C. Auer von Welsbach he has measured the arc spectrum from 2231 A to 7881 A. An earlier work by Eder[7] gives practically the same list of lines in the orange and red regions.

In general, the agreement between his two sets of results and those presented here is very good. Slight discrepancies, not accounted for, are the appearance in each list of wave lengths of faint lines not to be found in the other.

TABLE .1—Arc Spectrum of Yttrium

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5503. 474	4	A	5675. 303	4	A	5841. 898	1 1	B
5509. 936	3	A	5675. 642	1	A	5858. 824	1 n?	A
5513. 658	2	A	5686. 683	1 b	B	5871. 764	1	B
5521. 654	4	B	5693. 639	2	A	5876. 134	1 b, p?	B
5526. 729	1	B	5706. 758	4 R	A	5879. 953	1	A
5527. 589	5 R	B	5713. 845	2 b, n?	B	5893. 140	1 b, p?	B
5541. 647	1	B	5714. 918	2 b	B	5893. 929	1 b, p?	B
5544. 599	3	A	5720. 609	2	A	5902. 940	2	A
5546. 034	2	A	5723. 454	1	A	5939. 082	2 n	B
5550. 996	1	A	5726. 912	1 Er?	A	5945. 711	2	B
5556. 484	4 R	A	5728. 911	3	A	5949. 999	2	B
5567. 759	3	A	5730. 147	1 n	A	5956. 429	2 n	B
5577. 429	4 R	A	5740. 213	1	A	5972. 158	7 n	B
5581. 085	2	B	5743. 874	4	A	5987. 706	5 n	B
5581. 894	5 R	A	5746. 953	1 n	B	6003. 636	6 n	B
5590. 958	1	A	5765. 668	3	A	6009. 196	3 p?	B
5594. 126	1	A	5773. 937	2	A	6019. 920	5 n	B
5606. 345	3	A	5781. 696	1	B	6036. 647	4 n	B
5610. 352	1	A	5787. 740	2 g, coin	B	6053. 844	4 n	B
5619. 945	1	B	5797. 130	1	A	6072. 817	2 n	C
5623. 907	1	B	5800. 009	1 n?	B	6089. 373	2 n	C
5630. 144	6 R	A	5809. 289	1 p?	B	6096. 823	2 n	C
5632. 245	2	A	5812. 671	1	B	6107. 834	2 n	C
5632. 911	1	A	5818. 548	1	A	6114. 729	2 n	C
5641. 812	<1	B	5819. 258	1 b, p?	E	6127. 387	1 n	B
5644. 704	4 R	A	5820. 023	1 b	E	6132. 156	7 n	B
5648. 490	4 R	A	5821. 879	2 Er?	A	6135. 056	2 p?	B
5660. 909	1	B	5823. 774	1 I, p? La?	A	6138. 417	2	B
5662. 949	7 R	A	5832. 255	2	A	6148. 454	6 n	B
5669. 229	1	A	5838. 060	1 1	A	6165. 142	6 n	B

[6] Kaiser, Akad. der Wiss. Sitz. Wien., 125, IIa, p. 383; 1916.
[7] Kaiser, Akad. der Wiss. Sitz. Wien., 124, IIa, p. 118; 1915.

TABLE 1.—Arc Spectrum of Yttrium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6182. 250	4 n	B	6664. 378	3	B	7191. 628	2	B
6191. 719	4	A	6687. 575	4	A	7195. 942	1	B
6199. 859	2 n	A	6691. 848	2	B	7229. 119	1	E
6217. 981	2 n	B	6694. 749	2	B	7264. 186	2	C
6222. 572	2	A	6699. 259	2 La?	B	7330. 641	1 d?	C
6236. 719	2 n	B	6700. 707	3	A	7346. 444	2	A
6251. 039	2 n?*	E	6713. 195	2	A	7398. 871	1 b	C
6275. 013	2 n, Er?	B	6735. 991	2	A	7442. 258	1	D
6295. 489	2 n?*	C	6793. 694	4	A	7450. 286	2	B
6316. 308	2 n?*	C	6795. 402	2	A	7452. 978	1 b	E
6368. 120	1 n?*	C	6803. 152	2 b	C	7468. 365	1	E
6402. 016	2	B	6815. 147	2	B	7536. 696	1 b	C
6435. 029	6	A	6832. 474	1	B	7563. 061	2	B
6437. 173	2	A	6845. 226	3	B	7617. 744	1	D
6501. 263	2 n?	B	6858. 216	2	A	7622. 939	1	B
6503. 024	1 p?	C	6887. 214	3	A	7719. 893	2	E
6504. 579	1 p?	C	6895. 988	2	B	7724. 014	2	C
6518. 364	2 l, n?	B	6908. 266	2	B	7788. 390	1	C
6535. 873	2 l, n?	B	6933. 533	2	A	7796. 286	1	C
6538. 571	4	A	6950. 310	2	A			
						7802. 485	1	C
6553. 876	2 l, n?	B	6951. 662	1	A	7812. 132	1	C
6557. 360	3	A	6958. 005	1 La?	B	7855. 546	1	C
6572. 621	1 l, n?	B	6979. 860	2	A	7881. 868	2	A
6576. 859	2 Er?	A	7008. 946	2	B			
6584. 878	2	A	7009. 952	2	B			
6599. 588	1	C	7035. 188	2	B			
6613. 740	3	B	7052. 972	2	B			
6622. 511	2	B	7054. 323	1	B			
6636. 478	2 La?	B	7087. 71	1 h	D			
6650. 599	2	A	7127. 928	2	B			

2. LANTHANUM

In the regions studied, the spectrum of lanthanum is characterized by numerous lines of intensity 3 or greater. Superposed on the line spectrum is a banded spectrum which remains prominent out into the infra-red regions. In all, about 400 lines, including band heads, are tabulated below between the limits 5501 A and 9079 A. Both samples of lanthanum analyzed were very pure. Lines suspected as not being true lanthanum lines are appropriately marked. Among these, the two at 6262.30 A and 6645.19 A agree very closely with the strongest lines in the red region of the spectrum of europium.

Eder and Valenta [8] have measured on the Rowland scale the arc spectrum of lanthanum between the limits 5455 A in the green and 7066 A in the red. Shortly afterwards they also published measurements of heads of bands observed in the lanthanum arc.[9] A later work by Eder [10] using various compounds of lanthanum prepared by C. Auer von Welsbach resulted in the

[8] Kaiser, Akad. der Wiss. Sitz., Wien., 119, IIa, p. 39; 1910.
[9] Kaiser, Akad. der Wiss. Sitz., Wien., 119, IIa, p. 547; 1910.
[10] Kaiser, Akad. der Wiss. Sitz., Wien., 123, IIa, p. 2304; 1914.

determination of about 120 wave lengths in international units in the red from 6468 A to 8051 A. The stronger lines of his list are in close agreement with the wave lengths given below; but among his faint lines are many not to be found in the accompanying table. In like manner, Table 2 contains faint lines not to be found in Eder's list.

TABLE 2.—Arc Spectrum of Lanthanum

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5501.349	6 R	B	5823.829	4 R	A	6035.120	1 b, p?	E
5502.229	2	C	5827.550	3	A	6038.597	4 R	A
5502.656	2	C	5828.494	3	B	6041.587	2	A
5503.858	3	B	5829.729	4 R	B	6044.849	2 b, p?	B
5506.067	2*	B	5832.842	1	B	6046.050	1 b, p?	C
5515.315	2	B	5834.330	1	B	6061.430	1 b, p?*	C
5517.386	3	B	5835.931	1	B	6067.154	2	B
5529.895	1	B	5839.785	2	A	6068.703	4 R	A
5532.071	1	B	5845.021	4 R	A	6072.062	2	A
5541.284	4 R	B	5848.357	4 R	A	6074.007	1	A
5544.924	2	B	5848.949	2	A	6075.239	1	A
5565.396	3	B	5852.265	3	A	6084.931	3	A
5565.736	2	B	5855.562	4 R	A	6085.462	2	B
5566.938	2	B	5863.681	5 R	B	6087.950	1 p?	B
5568.482	4	B	5866.428	3 n	B	6092.271	2	B
5570.385	1	C	5869.554	3 n, p?	B	6100.364	3	A
5588.346	4 R	A	5869.965	2	A	6107.266	2	A
5600.065	5 n	C	5872.935	1 p?	E	6108.499	5 R	A
5602.559	5 n, p?	C	5873.986	2	A	6111.730	4 R	A
5626.148	4 n	C	5874.731	4	A	6120.339	1	A
5628.678	4 n, p?	C	5877.630	3	B	6121.274	1	B
5631.215	3	A	5877.984	3	B	6123.805	1	A
5632.055	3	B	5880.615	5 R	B	6126.084	4 R	A
5639.298	2	A	5892.664	1 p?	B	6127.051	3	A
5648.260	4	A	5893.592	3 n	B	6129.554	5 R	A
5652.518	2 n	C	5894.826	4 R	B	6134.403	5 R	A
5654.891	2 n, p?	C	5896.690	3 n, p?	B	6136.526	1	A
5657.743	4	A	5900.721	2 p?	A	6143.994	4	A
5671.560	3	A	5901.958	2	A	6145.339	3	A
5696.193	3 Gd?	A	5904.298	2	A	6146.552	2	B
5703.292	3	B	5917.622	4	A	6165.040	2	B
5712.412	3	A	5720.852	3 n	B	6165.716	5 R	A
5714.016	3	B	5723.969	2 p	A	6172.730	2	A
5714.547	2	B	5927.660	2 p	B	6174.192	1	B
5720.031	2	B	5928.495	2	B	6188.107	2	A
5727.298	2	A	5930.598	6 R	B	6203.540	2	A
5734.951	3	A	5935.263	3	B	6218.220	2	A
5740.647	6 R	A	5936.216	2	B	6219.522	1*	B
5742.946	3	A	5940.838	2	B	6233.522	2	A
5744.415	5 R	A	5948.236	2 n	B	6234.843	3	A
5761.840	5 R	A	5951.378	2 p	B	6236.230	2	A
5769.070	7 R	B	5960.583	2	B	6236.775	2	A
5769.368	7 R	B	5962.582	1	B	6238.586	3	A
5769.993	5 R	A	5965.331	1	A	6249.921	7 R	A
5789.234	6 R	A	5971.096	1 p?	E	6262.297	5 R Eu?	A
5791.331	7 R	A	5973.513	2	A	6266.030	4 R	A
5797.594	7 R	B	5975.785	3 l, n?	E	6273.780	1	B
5802.083	1 b, p?	B	5978.895	2 l, p?	B	6287.748	2	A
5805.767	5 R	A	5982.337	3	A	6288.584	2	A
5806.620	1 p?	B	5992.378	3	A	6293.571	4 R	A
5808.291	5 R	B	6007.367	4	A	6296.095	5 R	A
5810.372	1	A	6017.222	2	A	6305.463	2	A
5813.385	2	A	6025.108	1 p?	B	6307.265	1	A
5820.533	1*	B	6031.494	1 b, p?	B	6308.269	2	B
5821.998	6 R	A	6034.548	1 p?	B	6308.991	1 b*	B

TABLE 2.—Arc Spectrum of Lanthanum—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6310.224	2 b	B	6699.842	1	A	7257.187	2 b, n?	B
6310.939	3	A	6709.496	4	A	7270.075	2	A
6315.817	1	A	6714.091	2	A	7282.323	4	A
6318.290	2	A	6716.011	1	B	7289.296	2 n? *	B
6320.389	5 R	A	6718.664	1	B	7308.321	1 n? *	C
6325.919	5 R	A	6732.794	1	A	7320.901	1	B
6330.476	1*	A	6748.125	2	A	7322.001	1 n? *	C
6333.218	1 n?*	B	6753.039	3	A	7334.146	4	A
6333.833	2*	B	6774.268	4	A	7345.314	3	A
6337.915	2*	B	6776.785	1*	B	7354.840	1 n? *	B
6339.249	2*	B	6778.243	1*	B	7379.711	2	C
6356.438	2	B	6783.500	1 v*	B	7380.081	5 n	B
6358.130	3 Cu?	B	6796.707	1	B	7382.668	2 p	B
6360.242	3	A	6808.850	2	A	7403.576	7 n	B
6374.144	1	A	6813.655	1	A	7411.391	4 p	B
6375.110	2*	B	6816.290	1 b, d?*	B	7434.357	7 n	B
6380.558	1*	E	6821.530	2 v, h	B	7442.896	4 p, air?	B
6390.453	5 R	A	6823.785	3	A	7463.075	2	B
6394.242	6 R	A	6834.055	2	A	7465.276	5 n	B
6399.064	3	A	6837.912	2	A	7474.803	2 p?	C
6410.982	4	A	6859.044	1	B	7483.454	3	B
6417.223	1	A	6898.414	1 h*	B	7496.564	5 n	B
6443.086	1	B	6899.545	1 h*	B	7498.756	2 p?	B
6446.618	2	B	6902.117	1	B	7506.766	2 i, n?	B
6448.151	2	A	6903.073	1	B	7528.249	3 n	B
6450.331	2	A	6917.244	2	A	7539.203	2 p?	B
6454.508	3	A	6918.273	2	A	7560.161	3 n	B
6455.980	5 R	B	6925.235	3	A	7592.348	2 n	B
6468.438	2 b	B	6934.981	3	A	7612.959	1 p?	E
6485.544	3 h	C	6952.500	2 b	B	7624.922	2 n	B
6492.903	1 l, n?	B	6954.514	2	A	7657.867	1 n? *	B
6498.187	2	A	6956.176	1*	B	7664.331	2	B
6506.273	1 b, n?	A	6958.092	3	A	7666.731	1 n?	B
6519.332	1	A	6961.084	1	E	7691.079	1 n? *	B
6520.772	2 b, n?	A	6968.716	2	A	7698.830	1	B
6523.904	1	A	6976.837	1	A	7701.922	1 b, n? *	B
6526.976	4	A	6978.039	1	B	7716.687	1 b, p? *	B
6529.756	1	A	6994.473	2 n?	B	7724.360	1 n? *	C
6543.154	4	A	6996.867	2 b, p? Gd?	B	7737.780	1 n? *	C
6549.194	1	A	7011.196	2 n	B	7789.29	1 b, h	D
6554.136	1	A				7809.733	1 n	C
6555.054	1	B	7023.625	3 n?	B	7826.388	1	C
6555.950	1	E	7024.454	1	E	7841.856	2 b, n?	C
6565.415	3 b, h, Cu?	B	7032.009	2	B	7877.226	5 n	A
			7040.815	2 l, n?	B	7908.757	2 p?	B
6570.937	1	A	7045.933	4	A			
						7910.556	6 n	A
6578.518	4	A	7054.831	2 n*	B	7912.308	1 p? *	C
6582.207	1	A	7066.194	4	A	7945.013	5 n	B
6593.458	3	A	7068.323	3	A	7947.915	1 p?	C
6599.484	1 b	E	7070.799	2 n	A	7964.834	1	B
6600.166	2	A	7076.368	1*	B			
6605.090	1	A	7085.417	2 n*	B	7979.746	3 n	A
6607.676	1	E	7101.052	2 n	B	7983.304	1 p?	B
6608.253	3	A	7116.442	3 n*	C	8001.964	1 p?	B
6616.588	4	A	7131.680	2 n*	B	8014.830	2 n	A
6628.387	1	B	7147.480	2 n*	B	8019.541	1 p?	B
6631.218	1	A	7149.704	1 p?*	E	8050.250	2 n	A
6636.521	1 Yt?	A	7158.059	2	B	8051.360	1	B
6642.779	2	A	7161.192	3	A	8055.783	1 p? *	C
6644.389	3	A	7162.598	2 n*	B	8086.074	2	A
6645.188	2 Eu?	A	7179.029	2 n*	B	8122.213	1 n	A
6650.799	4	A	7193.674	2 b, n?	B	8129.808	1	E
6661.405	4	A	7211.015	2 n?*	B	8158.997	2	B
6671.402	2	A	7219.884	2	A	8196.017	1	C
6692.880	3	A	7225.235	2 v, n?	B	8203.391	1	C
6699.243	1 Yt?	A	7242.873	2 b, n?	B	8216.383	1 nir?	E

TABLE 2.—Arc Spectrum of Lanthanum—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
8233.054	1 h * air?	C	8519.15	<1	E	8703.16	<1 Cu?	E
8247.475	2	B	8526.66	2 n	B	8714.70	<1 n?	E
8316.031	1 *	B	8543.48	2	B	8720.40	1	C
8324.694	3	A	8545.428	3	A	8748.420	2	B
8346.547	3	A	8557.24	<1	E	8753.64	<1 n?	E
8379.728	2*	B	8563.54	2 n	B	8793.13	<1 n?	E
8453.86	1 n? *	D	8590.98	1	C	8818.95	1	E
8467.53	2 n?	C	8595.74	<1 b	E	8825.84	2	B
8476.483	2	A	8600.86	2 n	B	8839.67	1	E
8480.78	<1	E	8624.29	1	E			
						8957.70	1	B
8484.38	<1	E	8634.53	<1	E	8963.48	<1	E
8490.01	1 b, n?	C	8638.48	1 n?	C	9078.99	<1	E
8507.35	1	C	8672.13	2	B			
8513.55	1	C	8674.383	3	A			
8514.63	1	C	8676.50	1 n	E			

3. CERIUM

Table 3 contains about 1700 lines in the arc spectrum of ceriun between the limits 5500 A and 9025 A. Most of the lines are faint; that is, of intensity 2 or less. A band spectrum is indicated by the presence of a few band heads, but this feature does not display the prominence in cerium that it does in yttrium and lanthanum.

Using cerium ammonium nitrate and cerium chloride prepared by C. Auer von Welsbach, Eder and Valenta [11] measured the arc spectrum of cerium from 4800 A to 7253 A on the Rowland scale. A later work by Eder [12] yielded wave lengths between 6466 A and 8025 A, expressed in the international units. In the regions common to their work and that done at the Bureau of Standards there is very good agreement between the two sets of results.

TABLE 3.—Arc Spectrum of Cerium

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5500.91	1	B	5510.70	2	B	5520.20	1	B
5501.43	1	C	5511.19	1	E	5520.81	1	B
5501.79	1	E	5511.61	2	E	5521.05	<1	E
5502.80	1	B	5512.08	6	B	5521.88	2	B
5503.55	1	C	5513.14	2	B	5522.50	3	B
5504.19	1	C	5514.23	1	B	5523.01	1	B
5504.56	1	C	5515.23	1	C	5523.65	1	B
5505.11	1	C	5515.37	1	C	5524.42	2	C
5505.52	1	E	5516.07	2	B	5524.73	1	C
5506.04	2	B	5516.32	1	B	5525.58	1	E
5506.48	2	B	5517.40	2	B	5526.09	1	B
5508.04	1	B	5517.86	1	B	5526.78	2	B
5508.69	<1	C	5518.52	3	B	5527.15	2	B
5509.02	1	C	5519.02	1	B	5527.56	1	B
5509.44	1	C	5519.78	1	E	5527.93	1	C

[11] Kaiser, Akad. der Wiss. Sitz., Wien., 119, IIa, p. 531; 1910.

[12] Kaiser, Akad. der Wiss. Sitz., Wien., 123, IIa, p. 2308; 1914.

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5528.75	1	B	5568.79	1	E	5617.46	1	B
5529.13	1	E	5569.30	2	B	5618.18	1	B
5529.48	1	E	5570.48	1	B	5618.64	1	B
5529.90	<1	E	5570.94	2	B	5618.87	<1	E
5530.46	1	B	5571.61	1	B	5619.36	1	C
5531.18	1	B	5572.23	3	B	5619.69	1	C
5531.53	<1	E	5573.12	1	B	5620.38	2	A
5532.04	2	C	5574.36	<1	E	5620.77	<1	E
5532.92	1	C	5575.08	1	B	5621.76	<1	E
5533.21	1	B	5576.04	1	B	5622.23	1	B
5533.49	<1	E	5577.05	1	B	5622.65	2	B
5534.64	<1	E	5577.28	2	A	5623.00	2	B
5535.25	3	B	5578.29	3	A	5623.76	1	B
5535.84	1	E	5578.92	2	A	5624.84	1	B
5536.41	1	E	5579.24	1	B	5625.23	2	B
5537.26	2	B	5579.50	1	B	5626.01	1	A
5537.52	3	B	5580.60	<1	E	5626.73	1	A
5538.09	1	B	5582.58	2	B	5627.24	1	B
5538.51	1	C	5582.70	4	A	5627.63	1	A
5539.24	1	C	5583.87	1 d?	B	5628.17	2 d	A
5539.61	1	C	5584.72	3 d	B	5629.01	1	B
5540.57	2	B	5585.48	1	B	5629.71	1	B
5541.25	1	E	5586.72	2	A	5630.39	2	A
5541.59	<1	E	5587.24	<1	E	5630.98	1	A
5542.13	1	B	5588.12	1	B	5631.31	1	B
5542.77	2	B	5588.33	3	A	5632.07	1 d	B
5543.70	1	B	5589.25	1	A	5632.49	3	A
5544.12	1	C	5590.13	2	B	5633.09	4	B
5544.65	2	B	5590.52	2	B	5633.48	1	B
5545.24	<1	C	5592.16	1	A	5634.48	2	A
5545.50	1	C	5592.58	<1	E	5635.28	1	A
5546.16	1	B	5592.93	<1	E	5636.44	1	A
5546.52	1	B	5593.72	2	B	5636.91	1	E
5546.86	1	B	5594.17	1	B	5637.37	3	A
5547.48	1	A	5594.74	2	A	5638.18	4	A
5548.81	4	A	5594.97	3	A	5638.66	2 v, d?	A
5549.29	<1	D	5595.89	4	A	5640.14	2	A
5550.03	2	B	5596.54	1 d	B	5640.78	2	A
5550.64	1	B	5597.13	1	A	5641.43	1	B
5551.40	1	B	5597.96	3	A	5641.71	1	B
5551.63	<1	E	5598.96	3 d	A	5642.80	1	B
5552.30	1	B	5600.18	1	B	5643.88	1	B
5553.33	<1	E	5601.29	5	A	5644.29	1	B
5554.36	1	B	5602.09	<1	E	5644.72	2 b, d	B
5556.26	5	B	5602.79	1	A	5645.45	1	B
5556.95	3	A	5603.63	1	B	5645.96	1	B
5557.58	<1	E	5604.15	1	B	5646.60	3	B
5558.31	1	B	5604.39	2	A	5647.09	2	B
5558.65	2	B	5605.03	1	A	5647.74	1	B
5559.22	4	A	5606.13	1	A	5649.29	1	A
5560.06	2	A	5606.47	2	A	5649.95	<1	E
5560.96	1	B	5607.63	1	A	5650.59	3	A
5561.46	2	A	5608.48	1	B	5651.28	1	B
5562.21	2	B	5608.99	1	B	5652.20	1	B
5563.02	3	B	5609.44	2	B	5652.98	2	A
5563.74	<1	E	5610.27	4	B	5653.51	1	B
5564.26	3	B	5610.93	3	A	5654.21	<1	E
5564.99	5	A	5611.68	1	B	5655.17	6	A
5565.28	1*	A	5612.65	1	B	5656.21	2	A
5565.97	4	B	5613.71	3	A	5656.89	1 l, n?	E
5566.49	2	A	5614.22	1	B	5658.25	1	A
5567.06	<1	E	5614.75	4	A	5659.81	2	A
5567.52	1	B	5615.98	2	A	5660.48	1	B
5567.82	3	B	5616.53	1	A	5661.19	1	B
5568.23	<1	E	5617.12	1	A	5662.11	<1	E

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5662.72	1	A	5718.42	2 b, d?	B	5768.05	1	A
5663.24	3	B	5719.09	5	A	5768.94	5	A
5663.48	2*	B	5719.55	2	A	5769.95	2	A
5664.00	5*	A	5720.78	1 l, d?	C	5770.45	3	A
5664.68	2	B	5721.97	3	A	5771.55	1	B
5665.38	1	A	5722.62	1	A	5771.97	2	A
5667.14	1	B	5723.25	1	B	5772.23	3	A
5667.67	1	B	5724.47	1	B	5773.04	5	A
5668.00	1	C	5724.96	1	B	5773.58	3	A
5668.94	4	A	5725.85	4	A	5774.37	2	A
5669.97	6	A	5726.15	2	A	5775.03	2	A
5670.75	1	B	5727.27	2	A	5775.80	2	A
5671.42	2	A	5728.06	1	B	5776.23	2	C
5671.92	3	B	5728.63	1	B	5776.73	1	B
5673.73	1	A	5729.38	2	A	5777.26	1	B
5675.10	2	A	5730.46	1	A	5778.35	3 b, g coin?	B
5676.38	1	B	5730.81	1	B	5779.23	2	B
5676.89	3	A	5731.28	1	E	5780.22	2	B
5677.24	1	A	5731.91	1	B	5780.75	1	E
5677.76	5	A	5733.85	2 b, d	B	5781.32	<1	E
5678.33	1	A	5735.77	2 b, d	B	5782.43	2	E
5678.98	2	B	5736.58	1	B	5782.80	1	E
5680.27	2	B	5737.08	1	B	5783.99	3	A
5681.77	1	B	5737.49	1	B	5784.86	3	A
5682.22	1	A	5737.75	1	A	5785.76	1	B
5682.77	2	B	5738.32	2	A	5786.85	2	B
5683.12	2	A	5739.17	1 d	B	5787.21	2	A
5683.77	3	A	5739.63	2	A	5788.14	5	A
5684.38	1	A	5740.20	1 b	A	5788.58	1	A
5684.94	2	A	5741.13	1	A	5789.95	3 d, g coin?	B
5685.86	4	A	5741.92	1	B	5791.32	2	A
5687.82	1	A	5742.45	1 d	B	5791.67	2	A
5688.12	1	B	5743.52	5	A	5792.38	1	A
5688.48	2	B	5744.35	1*	B	5792.96	1	B
5689.90	2 b	B	5744.68	2	A	5794.32	1	A
5690.35	1 b, d?	B	5746.05	1	B	5794.79	2	A
5691.48	2	A	5746.48	2	A	5795.27	1	B
5692.12	2	A	5746.92	1	A	5796.05	3 d	A
5692.98	5	A	5747.36	1	A	5796.45	1	A
5694.05	1	B	5748.29	1	A	5797.40	2	A
5694.93	1 b, d?	A	5748.94	2	A	5798.09	2 d	B
5695.88	4	A	5749.36	1	B	5799.38	1	B
5697.02	5	A	5750.64	1	A	5799.80	3	A
5699.24	5	A	5751.20	1	B	5800.33	1	A
5699.92	<1	E	5752.12	1	B	5801.16	1	A
5700.45	<1	E	5752.51	2	A	5801.61	1	B
5700.86	<1	E	5753.03	1	A	5802.89	1	B
5701.51	1	B	5754.05	1	A	5803.23	1	A
5702.34	3	A	5754.71	1	A	5804.42	4	A
5703.25	3	A	5755.42	1	E	5804.96	1	A
5704.53	1 d	A	5756.00	1	B	5806.15	2	A
5706.21	1 b	B	5756.59	1 d	B	5806.53	1 d	B
5706.87	1	A	5757.48	1	B	5807.07	1	B
5707.44	2	A	5758.24	3	B	5807.50	1	A
5708.49	1	A	5758.79	1	A	5808.43	<1	E
5709.06	2	A	5759.71	<1	E	5809.35	1 d	A
5709.64	1	B	5760.16	1	A	5809.72	1	A
5710.07	1	A	5760.59	2	A	5810.73	3	A
5710.83	1	B	5760.97	2	A	5811.83	1	A
5711.45	3	A	5762.57	1	B	5812.93	6	A
5712.29	2	A	5763.00	2	B	5814.07	<1	B
5713.86	1	B	5763.36	1	B	5815.47	2	A
5714.33	1	A	5764.72	3 d	B	5815.91	1	B
5715.28	3	A	5765.34	3	A	5816.41	1	A
5716.49	3	A	5766.43	2 b, d?	B	5817.06	1	B

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5817.78	2	A	5872.94	2 d	B	5922.95	3	B
5818.80	1	B	5873.91	2	A	5923.55	1	B
5820.38	3 b, d?	B	5874.90	<1	E	5924.05	3	A
5820.80	1	A	5875.85	1	C	5924.90	2	A
5822.99	3	A	5876.44	1	B	5926.28	4	A
5823.46	2	A	5877.12	<1	E	5927.31	1	B
5824.60	1	A	5877.69	1	C	5927.76	1	B
5825.22	1 b, d?	C	5878.07	2	B	5928.32	4	B
5826.56	1	A	5878.94	3	B	5928.74	2	A
5826.88	1*	A	5879.92	1	C	5929.46	3	B
5827.25	2	A	5880.43	1	C	5929.84	3	B
5828.00	<1	B	5880.97	1	C	5931.71	1	C
5828.40	1 Cu?	B	5881.69	2	B	5932.17	2	B
5828.82	1	B	5882.69	2	B	5932.64	1	C
5829.33	1	B	5884.89	1 d	B	5933.05	1	C
5830.03	3 d	B	5885.82	1	B	5933.58	2	B
5830.67	1	B	5886.26	1	B	5934.43	5	B
5831.37	2 Cu?	B	5886.69	1	B	5935.44	1	C
5831.92	5	A	5887.55	2	B	5936.76	1	C
5832.29	1	B	5888.00	1	B	5937.69	4	B
5832.88	1 d	B	5888.50	2	A	5938.38	2 d	B
5834.25	2	A	5888.99	1	B	5939.80	1	B
5835.84	5	A	5889.60	3	B	5940.84	5	B
5837.66	1	B	5891.29	1	C	5941.51	3	B
5838.13	4	A	5892.48	2	B	5941.87	2	B
5838.88	1	A	5893.24	3	B	5942.66	3	B
5839.36	3	A	5893.90	1	C	5943.57	2 l, n?	B
5840.01	<1*	B	5894.32	1	B	5944.88	3	B
5841.59	<1	B	5894.93	2	A	5945.40	1	C
5842.11	1	B	5895.85	3 d, Na coin?	B	5946.23	1	C
5843.10	2	A				5947.03	1 d	B
5843.73	3	A	5896.34	3 b, l	B	5947.64	3	B
5844.36	2 b	B	5897.72	1	C	5948.19	2	B
5845.37	1	B	5898.10	2	A	5948.78	1 d	B
5845.98	3	B	5898.89	1	B	5950.23	1	B
			5899.23	1	B			
5846.73	1	A				5950.60	3	B
5847.61	1 v	B	5899.70	2	A	5951.21	2	B
5848.32	2	A	5900.66	2	B	5952.25	1	B
5848.86	2	A	5901.33	3	A	5952.88	2	B
5849.56	1 l	B	5902.65	2	B	5956.04	1	C
			5903.03	1	B			
5851.08	3*	E				5956.77	2	B
5853.07	3 b	A	5903.54	<1	E	5959.07	1	B
5853.34	3*	A	5904.74	1	C	5959.73	3	B
5853.68	3	A	5905.27	1 d	C	5960.17	1	B
5854.85	1	B	5906.00	2	B	5960.81	2 d	B
			5906.85	1 b, d	B			
5855.19	1	A				5962.61	1	E
5856.64	1	B	5907.49	2	B	5963.35	2	B
5857.12	3	A	5908.34	<1	E	5964.07	1	C
5857.60	1	B	5909.20	1	B	5964.67	2	B
5858.19	2	B	5910.00	5 R	B	5966.26	4 d	B
			5910.68	1	C			
5858.56	2	B				5967.36	1	C
5859.37	3	A	5911.28	<1	E	5967.72	1	C
5862.50	5	A	5912.25	1	C	5968.08	2	B
5863.86	1	A	5912.88	3 d	B	5968.60	1	B
5864.53	1	A	5913.75	1	B	5969.20	1	C
			5914.84	3	B			
5865.16	1	A				5969.80	1	B
5865.75	1	C	5915.57	1	B	5970.25	1	C
5867.89	1	B	5916.29	1	C	5970.75	1	B
5868.49	1	B	5916.68	1	C	5972.08	3	B
5869.32	1 d	B	5917.43	1	B	5972.80	2	B
			5919.06	1	B			
5869.97	1	B				5973.50	1 v	B
5870.34	<1	B	5919.43	1	B	5974.62	1 b	E
5870.85	1	B	5919.93	1*	C	5975.25	2	B
5871.61	4	A	5920.40	3	B	5975.90	5	A
5872.30	1	B	5921.32	1 b	E	5978.43	1	A
			5922.11	2	A			

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
5979.39	2 l, n?	A	6018.41	1	C	6069.46	4	A
5979.74	1	B	6018.83	2	A	6070.17	1	B
5980.56	1	B	6020.59	1	B	6072.00	3	B
5981.18	2	B	6021.24	1	B	6072.32	1	B
5981.83	2	B	6021.64	2	B	6073.07	1	B
5982.35	<1	E	6022.36	1	C	6073.90	1 b	C
5982.91	1	C	6023.14	1	C	6074.26	1	C
5983.57	1	B	6024.19	5	A	6075.16	1	C
5984.25	1	B	6025.28	2 d	B	6075.58	2	B
5985.40	1 v	B	6026.05	2 d	B	6075.91	2	B
5986.24	2	B	6027.16	2	A	6076.63	3	B
5986.66	1	B	6027.78	1	B	6077.16	2	B
5987.38	2	B	6028.28	1	B	6077.55	2	B
5988.29	1	C	6029.07	2 d	B	6078.44	1	C
5988.79	2	B	6029.72	1	B	6079.37	2	B
5989.37	3	B	6030.35	1	C	6080.37	2	A
5990.22	1 l, n?	B	6030.67	2 Cu?	B	6081.27	2	B
5990.85	2	B	6031.25	2	A	6082.08	2	B
5991.62	2	B	6032.10	1	B	6082.80	1	C
5992.06	<1	E	6032.53	1	B	6083.39	1	C
5992.64	3	B	6033.57	3	A	6083.93	1	C
5993.31	1 Cug?	C	6034.20	4	B	6084.90	1 d	C
5993.83	1	C	6034.59	2 d	B	6085.40	1	B
5994.29	1	C	6035.48	3	A	6086.62	2	B
5994.74	1	C	6035.85	1	B	6087.38	1	B
5995.35	4	B	6036.62	2	B	6087.62	1	B
5996.20	1	C	6037.07	1	B	6088.21	1	B
5997.00	3	B	6038.40	1	B	6088.88	3	B
5997.38	1	C	6039.05	1	C	6089.40	1	B
5997.77	1	C	6039.80	1	B	6089.65	2	C
5998.11	1	C	6040.59	2	B	6090.97	2	B
5998.46	1	C	6041.37	1	C	6091.74	1	C
5999.31	1	C	6041.92	1	C	6092.34	2	B
6000.17	2	B	6043.39	5	A	6093.19	3	B
6000.86	1	C	6044.14	1 l	B	6093.56	1	B
6001.83	4	B	6045.44	3	B	6093.83	1	C
6002.27	1	C	6045.88	2	B	6094.29	1	B
6002.68	1	C	6046.72	1 d	B	6096.96	1	B
6003.09	1	C	6047.39	4	A	6097.60	2	B
6003.66	2	B	6050.07	2 v	B	6098.34	5	A
6004.03	1	E	6051.30	1	B	6099.40	1	C
6004.50	1	C	6051.78	3	B	6099.77	2	B
6005.33	1	E	6052.60	2	A	6100.11	2	B
6005.85	4	A	6053.29	1	E	6100.79	1	B
6006.21	2	B	6053.94	1	B	6101.24	1	C
6006.80	4	A	6054.63	1	B	6101.56	1	C
6007.38	2	A	6055.30	1	B	6102.74	2	B
6008.47	1	B	6056.08	1	C	6103.42	2	B
6009.03	1	E	6056.45	1	B	6104.02	2	B
6009.63	1	B	6057.42	4 d	B	6104.84	1	B
6010.09	1	B	6057.99	3	B	6107.04	1	C
6010.44	2	B	6058.60	1	C	6107.79	1	E
6011.04	1	E	6059.32	2 d	B	6108.74	4	B
6011.55	1	B	6060.70	3	B	6109.72	1	B
6011.96	1	B	6061.67	1	B	6111.92	2	B
6012.31	1	B	6062.40	1	C	6112.90	1	C
6013.40	5	A	6062.75	1	C	6113.33	1	C
6014.06	2	B	6063.43	1	C	6114.27	1	C
6014.65	1	E	6064.05	1	E	6114.69	1	B
6015.44	1	B	6064.48	2	A	6115.15	1	B
6015.99	1	B	6066.23	1	B	6115.44	1	C
6016.56	2	A	6066.72	2	B	6116.47	1	C
6017.02	1	B	6067.02	2	B	6117.71	1	B
6017.28	1	A	6068.17	1	B	6118.56	2	B
6017.86	1	B	6068.65	2	B	6118.87	2	B

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6119.79	2	B	6190.07	1	C	6271.18	1	B
6120.63	1	C	6192.27	1	B	6272.05	4	A
6123.66	4	A	6192.92	<1	E	6273.71	2 b	B
6124.31	1	B	6194.21	1	C	6274.35	1	B
6124.98	1	B	6194.75	1	B	6275.32	1	B
6125.43	1	C	6195.27	2	B	6276.45	3	B
6126.09	2 v, d?	B	6195.55	2	A	6276.86	1	C
6128.54	1	C	6196.29	2	A	6277.10	1	B
6129.00	1	B	6198.04	2	A	6279.10	1	B
6130.15	2	B	6200.65	1*	B	6281.58	1 l	B
6131.13	1	C	6201.83	2 b	B	6282.85	1	A
6132.06	3 d	B	6204.83	1 b, d?	B	6283.57	1	A
6132.76	1 d	B	6206.74	1	B	6283.99	1	A
6133.24	1	C	6208.32	1	B	6285.75	2	B
6133.61	2	B	6208.99	3	A	6286.34	2	B
6134.58	1	B	6209.58	2	B	6287.14	1	B
6135.51	2	A	6211.05	2	A	6287.64	1	C
6136.59	1	B	6211.67	<1	E	6290.49	1	B
6137.23	2	B	6212.51	2	A	6291.42	1	B
6138.33	1	B	6214.11	1	B	6294.36	1 d	B
6139.03	3	B	6216.07	2	A	6295.58	3	A
6139.82	1	C	6216.83	2	A	6296.15	1	B
6140.63	1	C	6220.72	1 d	B	6296.99	1	B
6141.34	1	B	6221.33	1	B	6299.51	3	A
6141.88	1 l, d?	B	6222.28	1	B	6300.23	3	A
6142.92	2	B	6223.23	2	B	6302.15	1	A
6143.39	4	B	6223.65	3 d	B	6302.77	1	B
6146.42	3	B	6225.50	1 d	B	6304.01	1	B
6146.95	1 d	B	6226.88	1	B	6305.26	1	B
6147.85	2	A	6227.32	1 l	C	6306.63	2	A
6149.58	2	B	6228.24	2	B	6307.55	1	B
6150.20	1	B	6229.00	4 d	B	6308.08	1	C
6151.20	1 v, d?	B	6230.26	1	B	6308.64	1	C
6151.73	2	A	6231.43	1 d	B	6309.29	1	B
6153.24	1	B	6232.46	3	A	6310.03	3	A
6153.92	1 d	B	6233.79	1 Cu?	C	6310.53	1	A
6155.05	1 b, d?	C	6237.45	3	A	6312.58	1	A
6155.49	2	B	6238.71	2	A	6316.44	1	B
6156.75	2	B	6241.47	1	B	6318.00	2	A
6157.63	1	C	6241.91	2	B	6318.57	2	A
6158.14	1	C	6242.92	2	A	6320.82	1	B
6158.93	2	A	6243.93	1	B	6321.25	2	A
6159.82	3	A	6244.87	1 b, l	B	6321.61	1	A
6161.36	1	B	6247.80	1	C	6322.37	1	B
6162.14	2	A	6249.64	1	C	6322.87	1	B
6162.73	1	B	6250.32	1	B	6323.87	1	B
6163.20	2	A	6250.91	1	B	6327.46	1	A
6164.43	1	B	6251.66	1	B	6328.16	1	B
6164.70	2	B	6253.27	1	B	6328.89	1 b, v	B
6165.54	2 d?	B	6253.62	2	B	6329.43	2	A
6166.56	1	B	6254.72	1	B	6330.05	1	B
6167.88	2	B	6255.74	1	B	6330.92	1	B
6172.91	2 d, air?	A	6256.36	2	A	6331.27	1	B
6174.00	1	E	6257.98	2	A	6332.00	2	A
6174.51	1	C	6258.60	1	C	6334.12	1	B
6175.28	2	A	6259.11	1 Dy?	B	6334.83	1	B
6177.96	2	A	6259.35	1	B	6335.39	3	A
6178.39	2	A	6259.78	1	C	6336.29	1	A
6180.08	1	A	6260.36	1 d	B	6337.22	2	A
6182.23	1	A	6261.06	1	B	6338.28	1	B
6184.04	2 d	A	6262.05	1 b, d?	B	6338.73	1	B
6186.16	3	A	6264.26	2	A	6339.89	1	A
6186.91	2	A	6266.23	1	A	6340.69	3	A
6187.91	2	A	6269.80	1	A	6341.85	1	B
6188.46	1	A	6270.28	2	A	6343.96	3	A

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6344.87	1 1	B	6448.46	<1	E	6532.29	1	B
6345.82	1	B	6449.77	1	E	6534.49	2	A
6346.72	1 air?	A	6450.95	<1	E	6537.48	2 v	B
6347.35	1	A	6451.38	<1	E	6537.99	1	B
6348.28	1	A	6451.98	1	B	6540.34	1	B
6348.80	1	A	6453.86	1	B	6541.67	1 b, d?	C
6349.40	1	A	6454.92	1	A	6542.06	<1	E
6351.27	1	B	6456.84	1	B	6542.96	1	B
6351.59	1	B	6458.06	3	B	6543.60	1	B
6352.18	1	B	6458.54	<1	E	6544.46	2 b, Cu?	C
6353.52	1	A	6458.96	<1	E	6546.45	1 b	E
6360.23	2	A	6460.59	<1	E	6548.58	1	C
6366.60	1	B	6461.86	2	B	6549.20	1	C
6367.79	1	B	6462.77	1	B	6549.88	1	C
6369.19	2	A	6466.85	2	B	6550.09	<1	E
6370.60	1	B	6467.40	3	A	6551.69	2	A
6371.10	3	A	6468.46	1	C	6555.65	3	A
6372.48	1	A	6468.97	2	A	6559.40	1	B
6372.99	1	A	6470.96	1	A	6559.92	1	E
6374.82	1	B	6471.73	1	B	6560.75	1	B
6379.23	1	A	6472.54	1	B	6562.12	1	E
6379.75	1	A	6473.08	1	A	6562.98	1	E
6380.11	1	A	6473.67	4	B	6563.47	2	B
6383.13	1	B	6477.89	1	B	6565.71	1	E
6383.50	1	B	6478.53	1	B	6567.85	1	C
6386.16	2	A	6479.33	1	B	6568.52	2	C
6386.86	3	A	6480.75	1 v	C	6570.82	1	A
6390.32	1	A	6481.98	1 air?	A	6573.65	1	B
6390.66	1	B	6482.53	<1	E	6574.04	1	C
6393.02	2	B	6482.84	1 b	C	6574.45	1	B
6394.09	<1	E	6485.97	1	A	6575.52	1 b	B
6395.12	1	B	6487.56	1	E	6577.47	1	B
6396.26	1	A	6488.01	1	E	6579.09	2	A
6399.90	1	B	6488.68	1	E	6580.46	1	E
6400.66	1*	E	6490.97	2	A	6581.14	<1	E
6403.66	1	B	6494.59	1	B	6581.98	<1	E
6411.68	1	E	6494.93	2	C	6582.79	1	E
6412.85	1	B	6496.90	1	B	6583.45	1 b	E
6415.41	<1*	E	6497.92	1	E	6588.63	1 b	B
6416.39	1	B	6499.56	1	C	6589.34	<1	E
6418.06	<1	E	6500.42	1	B	6590.48	1	C
6419.06	<1	E	6501.82	1	C	6591.19	1	C
6422.91	1	B	6503.26	2	A	6592.32	1	B
6423.34	1	B	6504.06	1	A	6594.55	<1	E
6424.47	1	B	6506.22	1 b, v	E	6596.52	1	B
6425.30	2	B	6507.18	2	A	6597.00	1	B
6425.87	1	B	6507.74	<1	E	6597.57	1	B
6426.53	1	E	6509.01	2	A	6598.42	1	B
6429.04	1	E	6511.44	<1	E	6598.99	1	C
6430.07	2	A	6513.61	3	A	6599.61	2	B
6431.51	1 b, v	C	6517.28	2	A	6600.16	1	C
6431.92	1	B	6519.12	1	A	6601.57	1	C
6433.41	2	A	6521.51	1	C	6602.20	1	B
6434.38	2	A	6522.05	1	B	6603.32	1 b	C
6435.48	<1	E	6522.55	1	B	6604.06	1	C
6436.40	2	A	6525.33	1	B	6605.37	2	B
6438.16	1	B	6526.15	1	B	6606.33	2	B
6439.95	1	B	6527.03	1	B	6606.87	2	B
6440.45	1	B	6527.85	1	B	6608.31	1 b	E
6441.02	1	B	6528.76	1	B	6609.72	1	B
6442.08	1	B	6529.42	1	B	6611.13	1	C
6445.22	1	E	6530.17	1	B	6612.06	2	A
6446.16	2	B	6530.70	1 1	A	6613.20	1	B
6447.10	<1	E	6530.98	<1	E	6614.38	1	B
6448.00	<1	E	6531.80	1	B	6615.53	1	B

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6616.30	1 b, d?	C	6713.42	1 b, v	B	6856.53	2	B
6617.81	1	C	6716.41	1	B	6857.05	1	B
6618.84	<1	E	6720.32	2	B	6863.06	1	C
6622.98	2	B	6721.53	1	C	6865.68	<1	E
6623.72	1	C	6722.36	1	C	6867.15	<1 b	E
6624.39	1	B	6725.46	1 v	B	6867.98	1	B
6626.03	1	B	6726.52	1	B	6868.94	1	B
6626.50	1	B	6728.25	<1	E	6869.56	1	C
6627.50	1 l	C	6728.69	2	A	6871.07	<1	E
6628.88	3	A	6729.55	2	A	6871.75	<1	E
6633.32	1	B	6730.06	<1 l	E	6872.12	<1	E
6634.78	2	C	6733.21	1	A	6873.41	1	B
6636.06	2	B	6735.56	1	B	6873.86	1	B
6636.92	1	B	6736.79	<1	E	6875.43	1	C
6637.32	1	B	6743.48	<1	E	6876.97	1	C
6641.13	1	B	6744.03	<1	E	6878.26	1	B
6643.15	1	B	6744.70	1	B	6880.18	1	C
6645.01	1	C	6746.89	1	B	6882.49	<1	E
6646.77	1	B	6749.44	1	B	6883.41	<1	E
6647.38	2	B	6750.20	1	E	6885.56	1 b	B
6649.32	<1 b, l	E	6755.08	1	B	6886.33	1	E
6650.87	2	B	6757.12	1	C	6887.71	1	B
6651.40	1	B	6761.17	<1	E	6892.29	1	B
6652.75	3	A	6764.40	1	C	6893.64	2	C
6653.00	1	E	6766.92	<1	E	6894.55	2	C
6653.56	1	C	6767.65	1	C	6898.48	2	B
6654.29	2	C	6769.29	1	B	6899.07	2	B
6654.81	2	C	6769.72	1	C	6901.50	<1	E
6655.47	1	B	6770.15	1	C	6902.10	1	B
6655.98	<1	E	6771.12	<1	E	6903.11	1	B
6656.96	1 b	E	6773.33	<1 ·	E	6903.51	1	E
6657.71	1	B	6774.25	2	A	6904.56	1 l	C
6658.55	1	B	6775.57	1 Cu?	C	6907.83	1	B
6659.13	<1	E	6778.23	1	B	6909.31	1	B
6660.00	1	B	6780.15	1	B	6910.51	<1	E
6661.41	2	A	6780.72	1	C	6911.35	1 K?	B
6662.55	1	B	6785.06	<1	E	6912.24	1	C
6663.72	<1	E	6789.90	1	B	6914.18	<1	E
6665.65	2 b, l	B	6791.36	1	C	6914.77	1	B
6665.94	1	E	6792.61	1	C	6916.27	1	E
6666.57	1	B	6793.81	1	C	6919.27	1	B
6670.63	1	B	6794.68	1	C	6921.14	1	E
6675.53	2	A	6795.46	1	C	6924.77	3	A
6676.71	<1	E	6801.75	1	C	6927.32	1	B
6677.32	1	B	6803.20	1	C	6928.02	1	B
6679.84	2	A	6806.10	1	E	6931.31	1	B
6683.55	1	C	6807.83	2	B	6932.12	1	B
6684.83	<1	B	6808.89	1	B	6933.32	1	E
6685.30	<1	E	6811.72	1	C	6933.64	1	E
6685.70	<1	E	6812.99	<1	E	6934.02	1	E
6686.59	2	B	6815.29	1	C	6939.40	2	B
6687.34	1	E	6818.20	1	B	6941.97	1 b	C
6688.74	<1	E	6826.43	1	C	6943.04	<1	E
6689.25	<1	E	6829.37	1	B	6943.50	1	E
6689.71	1	B	6829.75	2	B	6944.37	1 b	B
6690.96	<1 b	E	6833.37	<1	E	6946.76	1 b, v	C
6691.93	<1 b	C	6834.21	1	C	6948.29	<1 b	E
6692.59	1	B	6839.98	1	E	6948.72	1 b	E
6694.35	1	B	6844.43	1 b	E	6949.57	1 b	E
6696.16	1 b, l	B	6846.78	2	E	6953.18	1	B
6700.67	3	A	6847.27	2	E	6953.54	1	E
6704.38	3 d	A	6848.76	<1	E	6954.70	1	B
6706.03	2	A	6849.21	1	B	6955.28	1	B
6708.07	1	B	6850.77	1	C	6956.28	1	B
6710.16	1	B	6853.61	2	B	6957.21	1	B

TABLE 3.—Arc Spectrum of Cerium—Continued

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
6957.75	1	B	7132.08	1	C	7397.76	2	A
6959.11	1	C	7136.05	<1	E	7401.21	1 b, n?	B
6959.68	1	C	7141.40	2	B	7414.86	<1	E
6960.69	2	B	7141.71	1	B	7417.93	1 v	B
6963.08	1	E	7150.20	2	B	7424.84	1 b, n?	C
6963.54	1	E	7151.66	2	B	7433.04	1	C
6966.32	1	B	7155.20	1	B	7438.55	<1	E
6968.70	1	E	7156.96	2	B	7440.45	<1	E
6969.16	<1 b	E	7162.40	<1	E	7444.46	1	C
6970.40	1	C	7163.77	<1	E	7462.29	<1	E
6972.33	1	B	7166.04	<1	E	7472.39	<1	E
6973.48	2	B	7166.71	<1 d	E	7486.53	<1	E
6981.24	1 b, 1	B	7167.43	<1	E	7500.68	1	E
6981.99	<1 b	E	7167.88	<1	E	7506.46	<1	E
6983.77	1	B	7170.12	<1	E	7508.12	<1	E
6985.98	2	A	7174.95	1	B	7509.43	1 b	B
6991.48	1	B	7177.43	1	B	7509.75	1	E
6992.50	<1	E	7182.26	1	B	7511.36	<1	E
6993.10	<1	E	7186.18	<1	E	7527.58	1 b, d?	E
6999.85	2	B	7189.40	1 l, n?	B	7528.85	<1	E
7001.56	<1	E	7191.70	1	B	7539.53	<1	E
7003.18	<1	E	7196.78	<1	E	7540.64	<1 n?	E
7004.85	<1	E	7201.51	1	B	7541.24	<1	E
7006.52	<1	E	7201.86	2	B	7551.25	1 n?	B
7009.16	<1	E	7203.58	1	B	7556.63	<1 b	E
7009.86	<1	E	7206.23	1	B	7562.47	1	B
7010.59	1	C	7208.09	1	B	7562.92	1 l, n?	B
7013.33	1	C	7210.66	1	C	7563.52	1	C
7014.36	<1	E	7213.95	1	C	7616.06	1	B
7014.71	1	B	7217.34	2	B	7646.07	1	C
7017.18	1	B	7231.20	1	B	7663.37	<1	E
7017.72	<1	E	7232.44	<1	E	7670.89	2	C
7018.73	1	B	7232.95	1	B	7671.19	<1	E
7024.70	<1	E	7233.96	1	B	7678.11	1	C
7028.72	1	B	7235.70	2 n	B	7682.47	2	C
7029.90	1	B	7238.37	2	B	7689.13	2	A
7030.96	2	B	7241.69	2 n	B	7702.85	1	C
7040.75	1	C	7252.72	2	B	7724.70	<1	E
7049.60	1	B	7257.58	<1 p?	E	7732.32	2	C
7052.93	<1	E	7259.38	<1 p?	E	7748.35	1	B
7054.41	1	C	7262.63	1 p?	B	7797.73	2	C
7057.85	1	B	7275.57	1 p?	E	7835.81	2	B
7058.56	1	C	7277.92	1 n	B	7842.57	2	B
7059.91	1	C	7279.93	1 p?	B	7844.92	2	B
7061.69	3	B	7287.10	1 p?	E	7850.00	1	A
7064.41	1	B	7288.03	1 p?	E	7851.25	2	B
7065.68	1	B	7296.15	<1	E	7857.50	1	A
7066.41	1	C	7301.40	1	B	7859.05	2	B
7068.18	1	B	7310.24	<1	E	7860.54	2	B
7071.56	<1	E	7310.86	<1	E	7864.49	1	B
7075.13	<1	E	7311.75	<1	E	7866.05	1	B
7075.71	<1	E	7313.40	1	C	7874.10	1	B
7086.31	3	B	7329.90	2	A	7879.67	2 n	C
7087.04	<1	E	7334.69	1	B	7899.03	2 n?	B
7105.01	1	C	7337.65	<1	E	7904.84	1 n?	B
7110.25	<1	E	7343.41	1	B	7913.43	1	B
7113.10	1	C	7345.57	<1	E	7924.04	2 b*	C
7114.65	1	B	7361.81	<1 b	E	7927.53	2 n?	C
7115.07	1	E	7362.38	1	B	7953.57	1*	E
7118.72	<1	E	7363.11	1	B	7964.50	1*	E
7120.07	<1	E	7372.49	<1	E	7972.34	2 b*	E
7120.82	<1	E	7379.64	<1	E	7975.49	2 b*	C
7121.30	1 d?	E	7383.71	1	B	8002.66	2	B
7122.05	<1	E	7390.42	1	C	8018.94	1 b*	C
7123.45	<1	E	7393.42	1	B	8025.57	2	A

TABLE 3.—Arc Spectrum of Cerium—Continued.

λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error	λ I. A.	Notes	Probable error
8066.97	1 n?*	C	8332.30	1 b	B	8516.24	1	B
8109.09	1	B	8336.89	1	B	8523.32	1	B
8114.53	1	D	8349.19	1	C	8526.88	1 l, n?	D
8116.70	1 b*	C	8352.39	2	C	8535.26	1	B
8120.32	2	A	8355.32	2	B	8539.04	1	B
8165.35	1	B	8358.05	1	B	8543.30	1	E
8171.32	1	B	8363.82	2	B	8545.40	<1	E
8175.35	1	C	8368.55	1	B	8548.13	1	C
8179.81	1 b	C	8371.90	2	B	8560.60	2	C
8195.28	1	B	8376.35	1	C	8564.56	1	B
8199.09	1	B	8381.02	1	B	8567.36	1	C
8215.50	1	A	8383.14	1	C	8575.56	1	B
8220.65	1	A	8386.22	<1	E	8583.87	2 b,l,Cu?	B
8223.69	2 b, d?	B	8387.71	<1	E	8612.62	2	B
8226.94	1	B	8396.20	2	D	8613.58	1	E
8234.12	3 b	B	8403.67	1	D	8633.25	<1	C
8237.73	1	B	8405.02	1	D	8636.40	1	B
8239.37	1	B	8408.65	1 b, Cu?	D	8647.59	2	B
8241.53	1	B	8417.96	2	C	8672.45	1	C
8245.10	2	B	8426.16	<1	E	8677.46	1	D
8246.79	1	C	8427.24	1	C	8702.32	1	C
8250.53	1	C	8441.05	1	B	8704.25	1	B
8251.21	1	B	8442.39	<1	E	8716.64	1	C
8252.52	1	B	8446.88	1	E	8756.26	1	C
8258.35	1 b	B	8455.97	<1	E	8772.08	3	B
8261.03	2	B	8459.98	1 b, d	B	8782.30	1	E
8276.36	1	B	8467.38	2 b	C	8810.77	1	E
8278.02	1	B	8475.78	1	B	8891.14	1	C
8296.06	1 n?	B	8483.34	1 b	B	8910.98	1	C
8299.84	<1	E	8488.21	1	B	8927.42	1	D
8300.58	2	B	8491.67	<1	E	8970.41	<1	E
8310.22	2	B	8495.64	3	B	8992.36	<1	E
8312.30	1	B	8503.57	1 b	B	8998.85	<1	E
8322.85	1 b	C	8511.16	1	C	9024.68	1	B
8327.58	1	C	8513.70	1 b	C			

IV. SUMMARY

The yellow, red, and infra-red regions of the arc spectra of yttrium, lanthanum, and cerium have been photographed with various concave gratings in the spectrograph of the Bureau of Standards. Plates specially sensitized with the dyes pinacyanol, kryptocyanin, and dicyanin were used for making the spectrograms. Two sets of materials were burned in copper or graphite arcs to furnish the luminous sources studied. These consisted of the chlorides of yttrium and lanthanum and the nitrate of cerium obtained from Eimer and Amend; and the oxalates of yttrium and lanthanum and the oxide of cerium obtained from the chemical laboratory of the University of Illinois, where they were prepared under the direction of Prof. B. S. Hopkins. The tables contain a total of about 2300 wave lengths, many of which are heads of bands. In yttrium about 175 lines were measured from 5003 A to 7882 A where the spectrum seems to end abruptly. In lan-

thanum about 400 lines were measured between 5501 A and 9079 A; and in cerium 1700 lines were measured between 5500 A and 9025 A.

To F. J. Stimson and Mr. Myers credit is due for assistance in the securing and reduction of many of the spectrograms, to Prof. B. S. Hopkins, of the University of Illinois, for the generous samples of materials used in the work, and to Prof. J. S. Ames, of Johns Hopkins University, for the loan of the several gratings with which some of the work was done.

PART II.—THE PREPARATION OF PURE RARE EARTH ELEMENTS

By B. S. Hopkins and H. C. Kremers

ABSTRACT

At the University of Illinois compounds of Ce, Sa, La, Nd, and Gd were extracted from sodium rare-earth sulphate, donated by the Welsbach Co.; and compounds of yttrium, dysprosium, and erbium were extracted from gadolinite obtained from Norway and Texas, and from an oxalate prepared from xenotime.

Cerium was removed from the Welsbach residues by boiling the neutral solution with potassium bromate to precipitate basic ceric nitrate. After removal of Ce, Sa was concentrated at the soluble end of a magnesium double nitrate series of fractional crystallizations, and La at the insoluble end of the series, the middle fractions of the series being used in the preparation of Nd. Gd was obtained from the fractions at the soluble end of the series, Sa being nearly all removed by adding bismuth magnesium nitrate.

The yttrium-group material was first freed from the cerium-group elements. It was then converted to bromate and subjected to a long series of fractional crystallizations. From the various bromate fractions, Y, Dy, and Er were prepared, respectively. Y probably contained not more than 0.005 per cent Ho and was reasonably free from other earths. The best samples of Dy contained some Tb and Ho; and the best Er fractions contained considerable Y and probable small amounts of other rare earths.

I. INTRODUCTION

The work upon the rare earths which has been in progress for several years at the University of Illinois has been concerned with both the cerium-group and yttrium-group elements. Of the cerium-group elements, compounds of samarium, lanthanum, neodymium, cerium, and gadolinium have been furnished to the Bureau of Standards for the accurate measurement of spectrum lines. These materials were practically all derived from the same source, which was a shipment of 182 kg of sodium cerium-group sulphates obtained through the courtesy of the Welsbach Co., of Gloucester, N. J., and its chief chemist, Dr. H. S. Miner. The early steps in the purification of compounds of these elements are identical, and consequently the process is described under the first elements, cerium and samarium, and the description for the other elements is taken up where each is separated from the general process.

The materials from the yttrium group include compounds of yttrium, erbium, dysprosium, and gadolinium. The sources of

the material were 10 kg of gadolinite which came from Norway and 55 kg of rare earth oxalates which had been prepared from xenotime and purchased from Drossbach & Co., Freiburg, Saxony. Later 100 kg of gadolinite were obtained from the deposit at Barringer Hill, Tex. The first steps in the purification of these materials are identical, since the elements of this group resemble one another closely in properties. When, however, the material was treated for some time by the method of fractional crystallization, separations began to appear, and each element was in turn separated from the general process. Accordingly, in this description the treatment of the ore and the first steps in the separation are explained under yttrium, while the discussion of the other elements is taken up at the point where each was removed from the general process.

II. THE CERIUM GROUP

1. CERIUM [13]

The rare earth residues obtained from the Welsbach Co. were chiefly the sodium double sulphates of lanthanum, praseodymium, neodymium, samarium, gadolinium, and cerium, with small amounts of europium and the yttrium-group elements. These double sulphates were boiled for a few hours with a 50 per cent sodium hydroxide solution until they were completely disintegrated. The mass was diluted and the resulting hydroxides filtered and washed with boiling water until free from sulphates. The hydroxides were dissolved in nitric acid, and the rare earths precipitated from hot solution by oxalic acid. After a thorough washing on a Büchner funnel with hot water, the oxalates were drained as dry as possible and dissolved in pure nitric acid. The resulting nearly neutral solution was heated to boiling and potassium bromate added in 10 g portions as proposed by James and Pratt.[14] When the liberated acid became strong enough to set free the fumes of bromine, lumps of marble were added to keep the solution neutral. Then the solution was boiled until the cerium present was thrown down as the deep yellow, insoluble basic ceric nitrate. This operation was continued until all but about 1 per cent of the cerium had been removed. This point is determined roughly by the intensity of the color of the precipitate formed in the hydrogen peroxide test for cerium and also

[13] This work was carried out in conjunction with Dr. Edward Wichers.
[14] J. Am. Chem. Soc., 33, p. 1326; 1911.

by the fact that the last portions of cerium are thrown down very slowly by this treatment.

In this manner almost chemically pure cerium was separated. About 1 per cent was left in the solution because if an attempt had been made to precipitate the last of the cerium in the same manner it would have been contaminated by other rare earths.

The basic ceric nitrate was filtered off and washed thoroughly with a 5 per cent solution of ammonium nitrate, which prevented the precipitate from becoming colloidal. The cerium material was then dissolved in nitric acid with the aid of a little alcohol and again precipitated as the basic ceric nitrate in the same manner as before. After another thorough washing the material was once more converted to the nitrate. A 20 cm layer of this solution showed no absorption lines, when viewed with a spectroscope.

The final purification consisted in precipitation of the oxalate in the presence of free nitric acid, followed by a thorough washing of the precipitate. This process was repeated twice more and finally the oxalate was converted to the oxide by ignition in platinum.

2. SAMARIUM [15]

The solution from which most of the cerium material had been removed, as just described, was boiled still further to remove the last traces of cerium, an excess of marble being present to keep the solution neutral. In this manner all the remaining cerium and a small amount of the other rare earths were thrown down. The boiling was continued until a small filtered portion of the solution failed to respond to the hydrogen peroxide test for cerium. When this point was reached, the residue, which consisted of a mixture of marble and ceric basic nitrates intermingled with some of the other rare earths, was filtered off. Then the remaining rare earths were precipitated from a boiling solution by hot oxalic acid solution. The precipitated rare earth oxalates were washed thoroughly first by decantation and then on a large Büchner funnel. The oxalates were dried in an air bath and ignited in an electric furnace and the resultant oxides dissolved in nitric acid. A quantity of nitric acid equal to that used in the solution of the rare earth oxides was neutralized by adding magnesium oxide. The two nitrate solutions were then filtered, mixed, and evaporated until crystals of the magnesium rare earth nitrate began to

[15] The samarium material was prepared by Dr. A. W. Owens, formerly of the Bureau of Standards while he was a student at the University of Illinois.

form on the surface. To prevent the formation of a crust on the surface as the solution cooled, a layer of water was added carefully and the dish left undisturbed for 24 hours. At the end of this time the solution was thoroughly drained off from the crystals and both crystals and mother liquor put through the process of fractional crystallization. Whenever the solution at the insoluble end no longer showed in the spectrum the absorption lines of neodymium, this dish was set out of the series and reserved for work on lanthanum and praseodymium. When the soluble end began to crystallize poorly, this portion was diluted, filtered, and the rare earths separated from other soluble salts by precipitation with oxalic acid. The fractionation was continued as long as samarium continued to appear at the soluble end.

When it became evident that the samarium had all been removed from the series, the oxalates from the soluble end were ignited and again converted into the magnesium rare earth nitrate by the method already described. The second fractionation was carried out in the same manner as before with the object of more completely separating samarium and neodymium. When the absorption bands of neodymium disappeared from any fraction at the soluble end it was set out of the series and the samarium precipitated by oxalic acid. When the samarium lines disappeared from any fraction at the insoluble end it was set out for the preparation of pure neodymium material.

The samarium oxalate, prepared as stated, contained appreciable amounts of gadolinium, some europium, and most of the yttrium group earths contained in the original monazite residues. To free the samarium from the yttrium-group elements the method of fractional crystallization of the magnesium double nitrate in 30 per cent nitric acid was used. After 180 fractionations in this manner it was found that practically all the yttrium earths had been removed. Double magnesium bismuth nitrate was then added at the soluble end of the series, as first proposed by Urbain and Lacomb.[16] The fractionation was now continued in the same manner as formerly, with the samarium coming out at the insoluble end, with the bismuth salt next, and the europium and gadolinium following in order at the soluble end. As the fractionation continued the concentration of the nitric acid solvent increased to 50 per cent or more, which probably aided the complete isolation of samarium. After 35 fractionations in this manner, the material at the insoluble end was thought to be pure

[16] C. R., 137, p. 793; 1903.

samarium, since no absorption lines other than samarium had been visible for some time. Accordingly atomic weight determinations, using the oxide to chloride ratio, were run on 6 fractions, as follows:

Fraction No.	Atomic weight
9	155.35
10	154.32
11	152.64
12	153.06
13	152.60
14	153.81

The lack of uniformity in the results and the high values were interpreted as indicating considerable variations in the composition of the fractions. Accordingly the fractionation was continued through 150 additional crystallizations, and then the atomic weights of fractions 32 to 43 determined by the same ratio. The values obtained in this second series were somewhat lower than in the first, but again there was a discouraging lack of checks upon duplicate analyses. Several considerations pointed to the fact that the oxide-chloride ratio was at fault. When the same material was used in determining the atomic weight by the chloride-silver ratio splendid results were obtained, showing that the material was uniform in composition and free from other salts. Eighteen successful determinations made on material taken from 14 different fractions gave extreme values varying between 150.49 and 150.40, with a mean of 150.43, which agrees with the accepted value 150.4.

The material sent to the Bureau of Standards was taken from these purest fractions, the final purification being accomplished by alternate precipitations as hydroxide and oxalate.

3. LANTHANUM [17]

Those fractions of the magnesium double nitrate crystallization which were set out at the insoluble end of the series, as explained in the preceding discussion, contained lanthanum with small amounts of praseodymium. These lanthanum-rich fractions were then removed and converted into the double ammonium nitrates and given a long series of recrystallizations. Lanthanum can best be separated from small amounts of praseodymium by means of the double ammonium nitrates. Since praseodymium, with possible small amounts of neodymium, would be the only other rare earths present here, a simple absorption spectrum analysis of the

[17] The preliminary part of the fractionation of the double magnesium nitrates was carried out by Dr. E. Wichers and the fractionation of the double ammonium nitrates was carried out by Dr. E. W. Engle.

solution would indicate the purity of the lanthanum. The purest lanthanum thus obtained showed no absorbtion bands when observed through a 10 cm layer of the concentrated solution. The final purification of the lanthanum material was accomplished by precipitation from hot solution with oxalic acid in the presence of free nitric acid; the precipitate was thoroughly washed, dried, ignited, and redissolved in nitric acid. This process was repeated twice more, the final treatment stopping with the oxalate, which was the material supplied for spectrum work.

4. NEODYMIUM [18]

The fractionation of the neodymium-rich portion of the double magnesium nitrate series from which the lanthanum had been obtained as described above was continued for some time. Since neodymium is more abundant than any other earth of this group, after the separation of cerium, the problem of obtaining relatively large quantities of neodymium of high purity is not difficult. The concentration of neodymium in the fractionation of the double magnesium nitrates is more rapid than that of any other earth whose isolation is effected by fractional crystallization methods. Thus if the fractionation of a series of high-grade neodymium material of several kilograms in weight is continued for a considerable length of time—e. g., some hundreds of fractionations—the middle fractions will consist of very pure material. All of the lanthanum and smaller amounts of praseodymium together with a high per cent of neodymium concentrate toward the least soluble end. The more soluble end will consist of a high per cent of neodymium of course, with the remainder composed mostly of samarium plus very small traces of gadolinium and europium. As fractionation continued in the above series the end fractions were removed from time to time. When it became apparent that no further concentration of the middle fractions took place the fractionation was discontinued. The oxide was prepared by the same method as that described under cerium and lanthanum.

5. GADOLINIUM

In the separation of the yttrium and cerium groups with either potassium or sodium sulphate, the terbium group of earths will be divided between the two groups. From this condition it follows that either or both the cerium or yttrium group may be taken as the source of gadolinium material. The gadolinium oxide

[18] The fractionation of the neodymium-rich material was carried out by Dr. E. W. Engle.

supplied to the Bureau of Standards was obtained from the cerium group. The raw material originally came from the Welsbach Co. as previously described.

In the fractionation of the double magnesium nitrates of the cerium group the increasing solubility of the earths is as follows: Lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, and terbium. The more soluble end of this series which very frequently does not crystallize well will contain mostly samarium, europium, gadolinium, and terbium. The soluble end of a large double magnesium nitrate series was mixed with bismuth nitrate and subjected to a long series of recrystallizations by other workers in this laboratory. The purpose in mind was the removal of the samarium at the insoluble end and the concentration of the gadolinium at the soluble end of the series. This separation was made completely by taking advantage of the fact that bismuth-magnesium nitrate is isomorphous with the magnesium rare earth nitrates and intermediate in solubility between samarium on the one hand and gadolinium on the other. The fractions obtained at the soluble end showed a high concentration of gadolinium. This material formed the basis for the work on gadolinium by Jordan and Hopkins.[19] These authors removed the bismuth and magnesium from this material in the regular way and subjected the oxide to a few precipitations with oxalic acid. The atomic weight of this oxide as determined by the permanganate method of Gibbs was 157.20. This value seemed to indicate very pure gadolinium. This material did, however, show some samarium absorption lines and the color of the oxide indicated some terbium. Since the atomic weight of samarium is 150.4 and terbium 159.2, these two values would neutralize each other. Bettendorf[20] discovered that if gadolinium oxide containing small amounts of terbium oxide was gently heated in hydrogen a pure white oxide resulted, and when again heated in air the oxide turned brown. The present authors found this to be the case with respect to the material at hand. This was then high-grade gadolinium with small amounts of samarium and terbium and perhaps traces of europium.

The usual methods of purification for the preparation of the oxide were used; that is, the complete removal of traces of bismuth with hydrogen sulphide and several alternate precipitations with freshly prepared ammonia and recrystallized oxalic acid.

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[19] J. Am. Chem. Soc., 39, p. 2614; 1917.

[20] Ann. Chem. Liebig., 263, p. 167; 1891.

III. THE YTTRIUM GROUP

1. YTTRIUM [21]

The gadolinite was pulverized in a ball mill, treated with an excess of HCl to which a little HNO_3 was added occasionally. After complete decomposition the silica was dehydrated and filtered off, then the rare-earth material was precipitated from a slightly acid solution with oxalic acid, both solutions being hot. The rare earth oxalate prepared in this way was mixed with the purchased oxalate derived from xenotime. The dry oxalates were converted to anhydrous sulphates by mixing with enough concentrated sulphuric acid to form a thick paste and then heating till fumes were no longer given off. The sulphates were dissolved in ice water and solid sodium sulphate sifted in, the solution being stirred continuously. The addition of sodium sulphate was continued until a 3-inch layer of the solution did not show the absorption lines of neodymium, when it was assumed that the relatively small per cent of the cerium group elements present was nearly all precipitated. The solid cerium-group sodium sulphates were filtered off and set aside, the solution containing the more soluble yttrium-group sodium sulphates was first treated with ammonium hydroxide and the precipitated hydroxides were washed very thoroughly to remove the sodium salts. The hydroxides were dissolved in hydrochloric acid and precipitated from hot solution by oxalic acid.

The first method of fractionation used was the method of fractional crystallization of the bromates as proposed by James.[22] The bromates were prepared by adding to a solution of the rare-earth sulphates a hot solution of barium bromate. The bromate solution was added slowly, the solutions being thoroughly agitated by a mechanical stirring device. The rare earth bromate solution was filtered off and subjected to fractional crystallization, the progress of the separation being observed by a direct vision spectroscope. After a few hundred series of fractionations had been carried out, it was found that certain portions of the series showed the color and absorption lines characteristic of various members of the group. As the fractional crystallization of the main series continued, certain portions, showing sufficient concentration of the individual earths, were set out of the main series forming a number of smaller subseries, whose treatment was

[21] The preliminary purification of yttrium material was done by Dr. J. E. Egan and other workers.
[22] J. Am. Chem. Soc., 30, p. 182; 1908.

continued for the purpose of further purification of the elements present.

The richest yttrium material selected from the fractional crystallization of the bromates was precipitated by oxalic acid, ignited to the oxide and the dry oxide, mixed with the calculated amount of chromic acid in an 8-liter round-bottom Jena flask. After thorough mixing, a small amount of water was added, when a violent reaction took place. Water was then added until the flask was about half full, then a 10 per cent solution of potassium chromate was added with shaking, until a faint cloudiness indicated that a permanent precipitate had begun to form. The material was then heated to boiling on a sand bath, a lively current of steam was passed into the solution to prevent the precipitate from collecting on the bottom and 10 per cent solution of potassium chromate was added drop by drop from a separatory funnel. The amount of chromate added was determined by the size of the precipitate desired. After adding the precipitant, boiling was continued for from one to two hours, the steam and burners being so regulated that the volume of solution remained constant. Finally, the material was cooled, the precipitate filtered out, dissolved in hydrochloric acid, a few cubic centimeters of alcohol added to reduce the chromate, and the rare earth precipitated with oxalic acid.

The chromate method of fractional precipitation was found to be efficient for removing from the yttrium material all of the rare earths present except erbium and holmium. From this treatment nearly 400 g. were obtained, with an average atomic weight of 90.3, as determined by the oxide to sulphate ratio. The absorption spectra of this material showed considerable holmium and erbium but none of the other rare earths.

Purification by fractional precipitation with dilute ammonia was carried out on two series of salts. One was obtained from the best fractions of the chromate fractionation (called the H series) and the other included 246 g of yttrium oxalate prepared in a similar manner, but showing no holmium lines (called the E series). In both series the rare earth chlorides were dissolved in water and diluted largely. Then 2 or 3 liters of ammonia of approximately 0.01 N strength were added. Under these conditions no precipitate appeared when the solutions were first mixed but on standing several hours a cloudiness appeared and after 24 hours a slight precipitate collected in the bottom of the flask.

After the precipitate was filtered out and purified the filtrate was evaporated to its original volume and the process repeated. The H series was fractionated 42 times in this way and the E series 37 times, the average fraction weighing about 3.1 g. The fractions of the H series below number 30 showed a constant atomic weight of 89.9, with holmium lines still prominent, but very little erbium. The E series shows an atomic weight of 88.7 in the fractions below number 25, the lower value being attributed to the absence of holmium, which the ammonia precipitation does not remove efficiently. The low atomic weights found are probably due to the fact that the values were obtained by a method which gives lower results than the oxide to sulphate ratio.

The purest fractions from both the E and H series of ammonia precipitations were further purified by fractional precipitation with sodium nitrite following in general the method of Holden and James.[23] This method consists in adding a strong solution of sodium nitrite to a dilute solution of rare earth material which has been carefully neutralized, and then boiling for a time, usually about one hour. It was found that the purification took place somewhat more rapidly if the rare earth solutions were sufficiently dilute so no precipitate formed when the ammonia was added. On boiling, the precipitate appeared. After standing some hours, the precipitate was filtered out, dissolved in nitric acid and purified, while the mother liquor was again fractionated. The best material from the H ammonia series was fractionated as the N series, which was split into 8 fractions, the last 4 of which showed an entire absence of color, while the first 4 fractions showed a decreasing pink color, indicating that erbium was concentrated in the first precipitates. Fractions N_3, N_4, N_5, and N_6 showed a constant atomic weight of 88.8 by the Gibbs method, while fractions N_7 and N_8 gave a value of 87.6. In spite of the fact that N_3 and N_4 showed a very faint pink tint, it was concluded that fractions N_3, N_4, N_5, and N_6 were presumably more nearly uniform than the last 4 fractions.

The fall in atomic weight shown at N_7 was thought to be due to the presence of some more basic material such as scandium or sodium. No trace of scandium was revealed by test with a saturated K_2SO_4 solution. The presence of sodium in these last fractions was considered probable because in the method of fractionation the mother liquor becomes heavily loaded with sodium salts. Accordingly N_7 and N_8 were very thoroughly purified by

[23] J. Am. Chem. Soc., 36, p. 1419; 1914.

alternate precipitations with ammonia and oxalic acid, together with two precipitations with ammonium sebacate. In spite of these steps the atomic weight of fractions N_7 and N_8 remained unchanged, and no explanation has yet been made for this peculiar fact. To prevent the possible use of material of lower atomic weight, fractions N_7 and N_8 were set aside and fractions N_3, N_4, N_5, and N_6 were combined, giving 106.2 g of material of average atomic weight of 88.87. This material was fractionated again by the nitrite method as series O, six fractions being obtained. The first 2 fractions showed the concentration of the erbium in the faint pink color and atomic weights 89.18 and 89.42, respectively. Fractions O_3, O_4, O_5, and O_6 were white, with atomic weights from 88.69 to 88.42.

A quantity of yttria corresponding to 37 g of the oxide was collected from the best fractions of the E ammonia series. This was split into five fractions by the sodium nitrite method forming series R. All of the fractions were pure white and showed a constant atomic weight, the values obtained varying between 88.58 and 88.40, which is only slightly more than the probable experimental error of the Gibbs method. Both these fractions and the O fractions showed very faint holmium lines when viewed through an accurate spectroscope looking through a 5 cm layer of concentrated solution. By comparison of this line with a standard holmium solution it was estimated that the amount of holmium present could not exceed 0.005 per cent.

The work of preparing the pure yttria was performed by Egan and Balke,[24] and by Hopkins and Balke.[25] Additional details are to be found in these papers.

Of the fractions prepared as described, O_4, O_5, O_6, R_3, R_4, and R_5 were used for the determination of atomic weight as described by Hopkins and Balke. Portions of the same material were used by Kremers and Hopkins[26] for the determination of the atomic weight by the chloride to silver ratio. The value obtained by the latter method, 89.33, has been accepted by the International Committee.[27] The material supplied the Bureau of Standards was taken from the mixed O_{4-6} fractions.

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[24] J. Am. Chem. Soc., 35, p. 365; 1913.
[25] J. Am. Chem. Soc., 38, p. 2332; 1916.
[26] J. Am. Chem. Soc., 41, p. 718; 1919.
[27] J. Am. Chem. Soc., 41, p. 1881; 1919.

2. DYSPROSIUM

The dysprosium material came entirely from the gadolinite and xenotime oxalate previously mentioned. From the main series of bromate fractions there were set out subseries C and D, as described by Engle and Balke.[28] These were further fractionated as the bromates for the concentration of dysprosium. After a long series of fractionation, series D indicated a high concentration of dysprosium collecting toward the middle fractions. Small amounts of neodymium and praseodymium had continually collected toward the less soluble end and were removed from time to time. Likewise the fraction showing stronger holmium bands had been removed from the more soluble end from time to time. Series C, which was composed mostly of dysprosium and holmium, with very small amounts of terbium and other earths, after a long series of fractionation indicated a concentration of high-grade dysprosium in the less soluble end.

The dysprosium-rich material from series D was then converted into a nitrate series. Bismuth nitrate was also added to the nitrate series with the hope that in the course of the fractionation the bismuth would aid the separation of the small amounts of terbium from the dysprosium. After 50 series of fractionations no marked separation had taken place and the series was converted to the ethyl sulphates.

The oxides obtained by Engle and Balke[29] from the simple nitrate series were dissolved in the calculated amount of ethyl sulphuric acid which was 0.63 normal. The neutral solution so obtained was warmed gently under diminished pressure until quite concentrated and then air was blown over the surface until crystals began to form. The series was then fractionated in the usual manner, using absolute alcohol as a solvent, since the ethyl sulphates hydrolyze badly in aqueous solution, especially if a trace of free acid is present. In dissolving the crystals it was necessary to use a steam bath at a temperature no hotter than the hand could bear with comfort. If precautions are taken to prevent the hydrolysis of the ethyl sulphates, this method of fractionation is found to be very useful, since there is much less tendency to form supersaturated solutions than in a bromate or nitrate series, and in addition the separation of dysprosium is quite satisfactory. After 20 series of fractionation as the ethyl sulphates, series D indicated that practically all the neodymium

[28] J. Am. Chem. Soc., 39, p. 53; 1917.
[29] For detailed description, see J. Am. Chem. Soc., 39, p. 53; 1917.

and praseodymium had been removed at the least soluble end and the dysprosium-rich fractions contained traces of terbium.

The dysprosium-rich fractions of series C were also converted to the ethyl sulphates and fractionated for some time. High-grade dysprosium material, with some holmium and traces of terbium, was obtained from this series. At this point all fractionation of the dysprosium material was discontinued by these workers and their time directed toward the accurate determination of the atomic weight of dysprosium.

The further purification of this dysprosium material was later continued as published by Kremers, Hopkins, and Engle.[30] Series C as left by the former workers contained a fraction of 1 per cent of terbium with slight amounts of neodymium and praseodymium toward the less soluble end. Holmium was contained in all the fractions. This series was fractionated 65 times. Practically all of the neodymium and praseodymium had been removed. The color of the oxide indicated slight amounts of terbium still present. The holmium was not removed by this method.

Series D contained besides the dysprosium only traces of terbium. After 60 series of fractionations small amounts of terbium still remained, although a considerable amount had concentrated toward the least soluble end.

The dysprosium oxide was prepared as follows: The alcoholic solution of the ethyl sulphates was diluted with water, a few cubic centimeters of dilute sulphuric acid added, and the solution heated to boiling and filtered. The dysprosium was then precipitated with oxalic acid. Several alternate precipitations with ammonia and oxalic acid were given. The ammonia precipitation was carried out by passing ammonia gas over the dilute nitrate solution and agitating until precipitation was complete. The hydroxides were washed by decantation until they became colloidal and then dissolved in nitric acid preparatory to the oxalate precipitation. A hot dilute solution of oxalic acid was added to the hot nitrate solution up to the point where precipitation began. Upon allowing the solution to cool a crystalline precipitate was obtained, which was easily washed. The washed oxalate was dried and ignited in platinum if another ammonia precipitation was desired. The oxalic and nitric acids here used were especially purified as described in the published work.[31] The oxide supplied for the spectroscopic examination was taken from the best fraction of series D.

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[30] J. Am. Chem. Soc., 40, p. 598; 1918.

[31] Loc. cit.

3. ERBIUM [32]

During the fractionation of the main bromate series of the yttrium group several of the individual fractions rich in erbium were removed from time to time and made up into series F, as described by Engle and Balke.[33] The fractionation of series F bromates was continued by these workers for some time, the object in view being to concentrate erbium. Finally several fractions were obtained composed only of erbium and yttrium, The erbium content was approximately 20 per cent. The fractionation of the bromates was then discontinued and the greater share of this material was subjected to other fractional methods with the hope of obtaining erbium of a high grade of purity. This latter work was undertaken by Wichers, Hopkins, and Balke.[34] The basic chloride method of Drossbach [35] was reported to give strikingly rapid results. Dr. Wichers applied this method to erbium-yttrium material of atomic weight 104. The yttrium and erbium fractions obtained had atomic weights of 95.9 and 110.6, respectively. These results, although good, were not as striking as claimed by Drossbach. The cobalticyanide method of James and Willard [36] was then tried on an erbium-yttrium mixture of atomic weight 108.5. Eleven fractions were obtained, the first and last atomic weights being 123.0 and 89.2, respectively.

Fractional precipitation with sodium nitrite has been used quite successfully by Hopkins and Balke [37] for the purification of yttrium. Dr. Wichers applied this method to a material of atomic weight of 108.5. Two series of precipitations were made, the erbium-rich material obtained from the first series being used in the second series. The best erbium material obtained in the second series of precipitations had an atomic weight of 142.9. It was apparent that none of the above methods could compare in efficiency to the nitrate fusion method.

In the fractionation of the bromates of an erbium-yttrium mixture several fractions rich in erbium and far removed from holmium on the one hand and thulium on the other had been obtained. A series of 32 nitrate fusions on this material gave the following fractions, with approximate atomic weights as indicated:

32 H	32 I	32 K	32 L	32 M	32 N	32 O	32 P
166.31	.....	.....	166.17	164.68	163.75	154.63	119.90

[32] Dr. Edward Wichers assisted in the preparation of erbium material.
[33] J. Am. Chem. Soc., 39, p. 53; 1917.
[34] J. Am. Chem. Soc., 40, p. 1615; 1918.
[35] Zeit. anorg. Chem., 76, p. 174; 1912.
[36] J. Am. Chem. Soc., 38, p. 1198; and 1497; 1916.
[37] J. Am. Chem. Soc., 38, p. 2332; 1916.

The 5 fractions richest in erbium were used by Dr. Wichers in the study of the oxide-chloride ratio for the atomic weight of erbium. A portion of fractions 32 N and 32 O, the best erbium material on hand at this time, was selected and purified to supply the oxide for the Bureau of Standards. This material was composed of only erbium and yttrium. It was purified in essentially the same way as the method used for dysprosium; that is, several alternate precipitations with ammonia and oxalic acid and final ignition in platinum.

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